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<b>(54) Title:</b> KAOLIN CLAY PIGMENT FOR PAPER COATING AND METHOD FOR PRODUCING SAME		
<b>(57) Abstract</b>  <p>A kaolin clay pigment comprises a coarse kaolin clay or a blend of a coarse kaolin clay with a fine kaolin clay. The kaolin clay is defined into a coarse fraction and a fine fraction. The fine fraction is discarded and the coarse fraction generally will have "blocky" particles at its coarse end and "platy" particles at its fine end with an overall shape factor greater than 12. If the defined coarse fraction is fluid at 65 % to 75 % solids, then it is used by itself as the kaolin pigment. If it is not fluid, it is blended with a fine kaolin clay in amounts ranging from 0.1 % to 30.0 % by weight of the blend. The coarse fraction has a Hinckley Crystallinity Index greater than 0.6 and the fine kaolin clay has a Hinckley Crystallinity Index less than 0.5. The pigment has a G.E. brightness of 90.5 and a particle size distribution such that at least 90 % by weight of the particles has an e.s.d. <math>&lt; 2 \mu\text{m}</math> and 30 % by weight of the particles has an e.s.d. <math>&lt; 0.25</math> microns. At 65 % to 75 % solids, the Hercules viscosity is greater than 250 rpm at 18 dynes and when used in a coating formulation, exhibits improved sheet brightness, sheet gloss, sheet opacity and print gloss.</p>		

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TITLE OF THE INVENTION

"KAOLIN CLAY PIGMENT FOR PAPER COATING AND  
METHOD FOR PRODUCING SAME"

1. Field of the Invention

This invention relates generally to kaolin clays and, in particular, to a kaolin clay pigment comprising a coarse kaolin clay or a blend of a coarse kaolin clay and a fine kaolin clay component with improved rheology properties, i.e., Hercules viscosity greater than 250 rpm at 18 dynes, for a high percent solids coating clay slurry, i.e., 65% to 75% solids, for coating groundwood or free sheet paper, with improved physical and optical properties.

2. Background Of The Invention

Kaolin clay pigments are obtained from kaolin. Kaolin is a type of rock formed through weathering or hydrothermal alteration of feldspar or mica minerals to kaolin minerals, or a sedimentary rock containing a high concentration of kaolinite particles or grains. Sedimentary kaolin rocks contain mostly clay or silt sized particles of kaolin minerals and fine and coarse particle size impurities. Some of the impurities (e.g. fine ferruginous or titaniferous impurities) impart undesirable color to the clay. Other impurities have an undesirable effect on the rheology of the kaolin, and still other impurities are coarse particles called "grit" that are generally above 45 microns which may cause scratching and/or abrasion if used in most applications.

The most common kaolin mineral is a naturally occurring hydrated aluminate silicate known as kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ). Kaolinite is the primary mineral in the kaolin clay widely used in the paper industry as fillers and/or coating pigments. Kaolin is also called china clay or hydrous kaolin. Its particles occur over a range of sizes and aspect ratios. Aspect ratio can be defined as the diameter of a kaolin particle divided by its thickness. Thus, a kaolin crude will not contain particles of a single size, such as, for example, particles all of which are 2 microns. Typically, a degritt (where 45 micron

particles are removed) kaolin crude will contain particles ranging in size from submicron or colloidal to particles 20 micrometers or larger.

Kaolins from different deposits, or even from different parts of the same deposit, can vary widely in the content of impurities, particle size distribution, as well as shape of the kaolin particles. In general, kaolin particles finer than about 1 micrometer are composed of individual platelets, and particles larger than about 1 micrometer are composed of stacks or booklets of several platelets mixed with discrete platelets. Particle sizes of kaolins are conventionally determined by sedimentation using Stokes Law to convert settling rates to particle size distribution, and assume a spherical particle shape for the kaolin particles, hence, the use of the conventional term "equivalent spherical diameter (e.s.d.)" to designate particle size.

Kaolin clay pigments are widely used to coat and to fill paper products. It was formerly the practice to simply use relatively coarse kaolins to fill papers and to employ finer grades of kaolin to coat paper. In paper, the coarser kaolin fillers functioned primarily as a pulp extender. When used to coat paper, the finer kaolin pigments improve brightness of the paper, provide a smooth, ink-receptive surface, and improve gloss with improved print quality and aesthetic appearance.

The crude kaolin ores can be mechanically delaminated. Delamination is generally known as the process of splitting apart kaolinite stacks or booklets which contain a number of platelets into discrete platelets. One delaminating operation involves subjecting the naturally occurring kaolin stacks to shearing forces in an extruder, thereby reducing the kaolin stacks to discrete platelets. Another operation involves subjecting the naturally occurring kaolin stacks in an aqueous clay slurry to the cleaving or delaminating action of an attrition mill or a sand grinder. Reference may be made to U.S. Patent No. 3,615,806 of Andrew Torock and Thomas F. Walsh for a thorough discussion of the process of delamination of kaolin clay. The kaolin pigments which have been delaminated can be used in paper coating to improve the opacity as well as enhance the smoothness of the paper surface. See for example, U.S. Patent No. 3,171,718, Gunn et al.

Kaolin clay can also be thermally structured through a calcination process which irreversibly converts the kaolinite into a material called "metakaolinite". Calcination causes the kaolin particles to stick or fuse together into porous aggregate and results in a pigment with higher light scattering caused by a higher index of refraction and a higher amount of light scattering surface than a kaolin which is not calcined.

Hydrous kaolin ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) is white in color, has a fine particle size, and is relatively chemically inert, and, in addition to its low cost, makes it an ideal paper filler. Calcined (anhydrous) kaolin is also available for use as a filler and can impart greater opacity to paper than the hydrated kaolin. However, it has some serious disadvantages of being more abrasive than hydrated kaolin clays. Hydrous and anhydrous kaolin clays are used to coat paper.

The purpose of paper coating is to cover an irregular paper surface comprised of cellulose wood fiber with a pigment-binder formulation, that when dry, leaves a smooth and brighter surface ready for printing. It is common practice to use kaolin clay along with other mineral pigments, such as titanium dioxide and calcium carbonates, as a coating formulation comprising starch and/or latex.

U.S. Patent No. 4,241,142, Kaliski, et. al., assigned to Engelhard Minerals and Chemicals Corporation, discloses a novel clay pigment used in the production of dull and matte-finished coated printing papers. The novel clay pigment comprises a mixture of a coarse-size fraction of naturally-occurring kaolin clay containing a substantial proportion of kaolinite booklets in the particle size range of 2 to 5 microns e.s.d., and mechanically delaminated kaolin platelets in the particle size range of 2 to 10 microns.

A paper coating pigment comprising mechanically delaminated kaolin particles is disclosed in U.S. Patent No. 5,169,443 to Willis, et al. and assigned to Engelhard Corporation. This pigment possesses the opacification, smoothness and printability advantages of conventional delaminated kaolin pigments but have desirably low viscosity and gloss not characteristic of conventional delaminated kaolin pigment.

It is well appreciated in the art that kaolin clay pigments must have certain rheological and optical properties to be suitable for use in paper manufacture as paper coatings or paper fillers. The kaolin pigment must be available as a high solids suspension typically having a clay solids content of about 50% to about 70% by weight, but still exhibiting a viscosity low enough to permit efficient and economical pumping, mixability with other filler or coating components and application to the paper. Additionally, it is utmost importance that the kaolin pigment exhibit certain optical properties, namely high brightness, high gloss, and high opacity.

The influence of particle size distribution upon the optical properties of kaolin pigments has long been appreciated in the art. For example, in U.S. Patent No. 2,992,936, Rowland discloses that a kaolin clay product having the following particle size distribution (in terms of equivalent spherical diameter, e.s.d.) will consistently show improved brightness, gloss and opacity when used as a paper coating clay:

- 99 - 100% by wt. less than 5 microns e.s.d.
- 98 - 100% by wt. less than 4 microns e.s.d.
- 88 - 100% by wt. less than 1.7 microns e.s.d.
- 85 - 87% by wt. less than 1.5 microns e.s.d.
- 70 - 84% by wt. less than 1.0 microns e.s.d.
- 25 - 37% by wt. less than 0.5 microns e.s.d.
- 10 - 15% by wt. less than 0.3 microns e.s.d.

A "defining" process generally refers to the operation of separating and discarding a percentage of the fine fraction of a kaolin suspension. The defining operation can be carried out on a centrifuge where the kaolin suspension to be "defined" is supplied to the centrifuge and processed therein to separate the suspension into a coarse fraction and a fine fraction. A selected percentage by volume of the fine fraction generally is discarded, while the remainder of the fine fraction is admixed with the coarse fraction for further processing. The percent defining level refers to the volume percentage of the fine fraction which is discarded. For example, defining to a level of 40% means that 40% of the fine fraction from the centrifuge was

discarded and the remaining 60% of the fine fraction from the centrifuge was admixed with the coarse from the centrifuge for further processing.

In U.S. Patent No. 5,085,707, Bundy et al. discloses a defined and delaminated kaolin composition which functions superiorly in paper coating formulations, alone or blended with known coating clays, to improve the opacity, print gloss, sheet gloss, and printability of paper sheet coated therewith.

Superior rheology in coating formulations permits the paper coating equipment to run at higher speeds (which directly increase the productivity of existing coating equipment) or permits the formulation of coating colors at higher solids (thus reducing drying time and hence increasing the efficiency of drying equipment). Delaminated pigments in clay-water slurries and in paper coating color formulations have had substantially poorer high shear rheological characteristics (higher viscosity) than undelaminated pigments. Thus, with the use of conventional delaminated pigments, papermakers must balance the tradeoff between paper opacification (quality) and efficiency of production (productivity).

The aforesaid U.S. Patent No. 5,411, 587, Willis et al. discloses a novel mechanically delaminated kaolin clay pigment useful for light weight printed paper which possesses the opacification, smoothness and printability advantages of conventional delaminated kaolin pigment, but have low viscosity and gloss not of conventional delaminated kaolin pigments. This reference teaches subjecting the crude kaolin clay to delamination and terminating delamination when a predominant proportion of the original booklet particles have been parted along basal cleavages into discrete platelets but before significant attrition of platelets occur.

Coating color viscosity is a key issue with paper coaters facing capacity constraints. A clay water slurry has to be fluid at high solids, e.g., 60% to 70% solids. If not fluid, then the coating color viscosity has to be lowered, which is unproductive in a paper mill. A clay-water slurry that has equivalent viscosity to a comparable slurry at only 2-3% higher pigment solids represents an improvement of significant commercial importance.

Generally, papermakers seek to use clay coating pigments capable of forming clay-water slurries at 60-70% solids which have a low shear viscosity below 1000 cp, preferably, below 500 cp, when measured by the Brookfield Viscometer at 20 rpm. High shear viscosity is considered of special importance in evaluating a high solids clay slurry for coating purposes. The more fluid the slurry, the higher the rpm of the Hercules Viscometer at 18 dynes. High shear viscosity for these slurries should be such that they are no more viscous than a slurry having a Hercules end point viscosity at  $18 \times 10^5$  dyne-cm of 500 rpm, preferably 800 rpm, using the "A" bob. Those skilled in the art are aware that when using the Hercules Viscometer and measuring end points of 1100 rpm or higher, viscosity is reported in units of dyne-cm at 1100 rpm. It is conventional to use the abbreviated term "dyne". A "2 dyne" clay slurry is less viscous than a "9 dyne" clay slurry at a given solids level.

Some coating formulations involve a combination of different types of kaolin pigments, such as a certain percentage of calcined kaolin clay and a certain percentage of hydrous kaolin clay, which combination can result in "poor" dispersion of particles in that the two types of kaolin clay pigments may aggregate which may disrupt the coating structure, resulting in poor sheet optics, poor printability, or both. Additionally, many paper coating compositions comprise an abundance of fines, which tend to affect the optical properties of the sheet by improving gloss at the expense of sheet brightness for some grades and opacity.

There is a need in the industry for an improved kaolin clay coating pigment which provides a fluid, low viscosity coating at a high solids concentration for paper, particularly for light weight printed paper, such as groundwood or free sheet paper, and which provides for a highly glossy and smooth surface with good opacity, printability and sheet brightness.

#### Summary of The Invention

The present invention has met this need. The present invention provides a kaolin clay pigment with a controlled particle size distribution and a shape factor preferably greater than 12 and, more preferably, ranging between 12 and 20. This pigment comprises a coarse kaolin clay or a blend



of a coarse kaolin clay and a fine kaolin clay component, the fine kaolin clay ranging from 0.1 to 30% by weight, and preferably 10% by weight, of the blend. The coarse clay is made by subjecting a coarse crude kaolin clay to several beneficiation steps, such as 1) removal of the titanium impurities; 2) a size-fraction step; 3) a grinding step; and optionally, 4) a desliming step. The removal of the titanium impurities could be done by a floatation process, a selective flocculation process, a magnetic separation process, or a combination of any of these processes. Preferably, the titanium removal is done through a selective flocculation process or a superconducting magnetic separation process with or without chemical additives to improve titania removal. The processing of the clay to produce the coarse kaolin clay pigment will produce clay particles with a TAPPI (G.E.) brightness of at least 89.0 and a steep particle size distribution such that at least 90% by weight of the particles have an equivalent spherical diameter (e.s.d.) less than 2 microns and not more than 30% by weight of the particles have an equivalent spherical diameter less than 0.25 micron.

The fine kaolin clay component of the pigment composition of the invention is characterized as being "fluid" and "blocky" with a shape factor less than 12 and will comprise individual thick platelets (i.e., blocky particles). The fine kaolin of the pigment composition of the invention is preferably made from a selective flocculation technique or a superconducting magnetic separation process with or without chemical additives to improve titanium removal, has a TAPPI brightness of at least 89.0, and has a particle size distribution such that at least 90% by weight of the particles have an equivalent spherical diameter less than 2  $\mu\text{m}$ , and about 50-75% by weight of the particles have an equivalent spherical diameter less than 0.25  $\mu\text{m}$ .

The coarse kaolin clay is processed from feed material having a Hinckley Crystallinity Index greater than 0.6.

The fine kaolin clay component of the invention is processed from a kaolin feed material with a Hinckley Crystallinity Index less than 0.5.

The coarse kaolin clay is preferably produced by a defining process where the fine fraction is generally discarded and the coarse fraction is used

in the present invention. The coarse kaolin fraction may have "blocky" particles at the coarse end and "platy" particles at the fine end which may give an overall shape factor greater than 12. The amount of the "platy" particles at the fine end of the coarse fraction may range from about 10 to 25% and preferably 14 to 17% where the p.s.d. is less than 25 microns.

The kaolin clay pigment of the invention regardless of whether it comprises coarse kaolin clay or a blend of a coarse kaolin clay and a fine kaolin clay preferably has a shape factor greater than 12. The clay particles of this pigment have a G.E. brightness of 89.0 or greater; and a steep particle size distribution (p.s.d.) such that at least 91% by weight of the particles have an equivalent spherical diameter (e.s.d.) less than 2 microns and not more than 30% by weight of the particles have an equivalent spherical diameter (e.s.d.) less than 0.25  $\mu\text{m}$ . If the coarse kaolin clay does not provide these physical properties, then the fine kaolin clay component is blended with the coarse clay in an amount ranging from 0.1% to 30.0% by weight to produce these desired physical properties in the pigment of the invention.

The kaolin clay pigment of the invention is capable of forming a high solids coating clay slurry with "good" fluidity, i.e., a Hercules viscosity greater than 250 rpm at 18 dynes at a solids ranging from 65% to 75%.

When the kaolin clay pigment in slurry form is used in a coating formulation, for example, for coating groundwood or free sheet, it has shown to yield superior sheet brightness, sheet gloss, sheet opacity and print gloss when compared to a commercially available kaolin clay product or blend. For example, as a coating, the kaolin clay pigment of the invention gives a TAPPI (G.E.) brightness gain ranging from 0.1 and 2 units; a sheet gloss gain ranging from 0.1 and 4.0 TAPPI units; a sheet opacity gain ranging from 0.1 to 1.0 TAPPI unit; and a print gloss (75°) gain ranging from 0.1 and 8 units.

Although it may be known in the art to blend a coarse fraction kaolin with a fine fraction kaolin, it is not known to remove the fine particle fraction of a coarse kaolin and replace it with a fine kaolin clay whereby a shape factor control is used to achieve the desired rheology of a high solids coating slurry.

Therefore, it is an object of the present invention to provide a kaolin clay pigment for coating lightweight paper such as groundwood or free sheet paper grades having improved rheological properties for a high solids concentration in a water-clay slurry with improved physical and optical properties in the coated sheet.

It is a further object of the present invention to provide a coating composition for lightweight printed paper such as groundwood and free sheet paper grades comprised of a kaolin clay pigment which is comprised either of a coarse kaolin clay or a blend of a coarse kaolin clay and a fine kaolin clay whereby the kaolin clay pigment has a controlled particle size distribution and a shape factor greater than 12.

It is a further object of the present invention to provide a method for producing a kaolin clay pigment for coating lightweight paper with improved rheological properties for a high solids clay slurry.

It is a further object of the invention to provide a coating composition comprising a kaolin clay pigment comprised of a coarse kaolin clay or a blend of a coarse clay and a fine glossy clay which forms a high solids slurry which has "good" fluidity and low viscosity with improved gloss values on coated sheet.

These and other objects of the present invention will be better appreciated and understood in reading the detailed description of the preferred embodiments.

#### Detailed Description of The Invention

The kaolin clay pigment of the invention generally comprises a kaolin clay product which is a coarse kaolin clay or a blend of this coarse kaolin clay admixed with a fine kaolin clay, both of which coarse and fine kaolin clays are preferably processed from a sedimentary kaolin, such as a Georgia Cretaceous kaolin. The coarse kaolin clay is processed from a well crystallized kaolin feed material containing low-defect kaolinite with a Hinckley Crystallinity Index greater than 0.6, and the fine kaolin clay is processed from a poorly crystallized kaolin feed material containing high-defect kaolinite with a Hinckley Crystallinity Index less than 0.5.

The Hinckley Crystallinity Index was developed in 1963 by D. N. Hinckley to describe how well a crystal structure of a kaolinite is ordered. Reference is made to "Variability In Crystallinity Among The Kaolin Deposits Of The Coastal Plains Of Georgia And South Carolina" by D. N. Hinckley in *Clays And Clay Minerals*, 1963, vol. 11, 229-235.

The coarse kaolin of the kaolin clay pigment of the invention preferably is produced by the following process.

A coarse crude kaolin clay with a Hinckley Crystallinity Index greater than 0.6 is blunged in water with sodium hexametaphosphate as a dispersion agent to form an aqueous slurry having a solids level ranging from about 50% to 70% by weight, and preferably 60% solids by weight. Other dispersing agents can be used, such as, for example, soda ash, sodium polyacrylate, and other dispersants equivalent to sodium hexametaphosphate. The clay is degrittled, i.e. the coarse particles in the kaolin above 45 microns are removed by passing the slurry through a series of screens. The impurities, including iron and/or titania impurities, are removed from the kaolin clay through flotation, magnetic separation, or selective flocculation, or two or more of these processes.

In the flotation process, the slurry is conditioned with an oleic acid which coats the air bubbles produced in the float cells. The titania minerals adhere to the air bubbles and are floated out of the kaolin slurry. This results in an improved brightness in the kaolin pigment, i.e., a brightness gain ranging from about 0.1 to 3 units. In the magnetic separation process, a high intensity wet magnetic separator is used to remove the iron-bearing minerals from the clay slurry, which also results in a brightness gain ranging from about 0.1 to about 3.0 units. In the selective flocculation process, a high molecular weight anionic polymer preferably having a molecular weight in excess of one million, preferably, in the range of 10 to 15 million, and preferably is a copolymer of a polyacrylamide or polyampholyte.

After the impurity removal step, the clay is subjected to a Bird centrifuge where the clay is classified to a particle size distribution such that

generally 89% to 96% by weight of the particles have an e.s.d. less than 2  $\mu\text{m}$ .

After classification in a Bird centrifuge, the clay is subjected to a delamination process. Delamination, as used herein and as discussed hereinabove, refers to the operation of subjecting the naturally occurring kaolin stacks in the aqueous clay slurry to shearing forces thereby reducing the number of kaolin stacks and forming discrete platelets. In each example presented herein, delamination was carried out by subjecting the aqueous slurry of stacked kaolin particles to shearing action in a sand grinder. In the examples, the kaolin slurry was introduced into the sand grinder at about 4 gallons per minute to produce a particle size distribution such that 92% to 97% by weight of the particles had an equivalent spherical diameter less than 2  $\mu\text{m}$ .

The kaolin slurry is then subjected to a defining step. In each example presented herein, the defining step was carried out on a centrifuge. The kaolin slurry was transferred to the centrifuge and processed to separate the suspension into a coarse fraction and a fine fraction. In the invention, this fine fraction generally is discarded in that it has been found by the inventors that this fine fraction generally contains a large percentage of platy particles which caused the slurry to be highly viscous. This fine fraction generally consists of a great amount of ultrafine particles, i.e., less than 0.25 microns and removal of these ultrafines is referred to as a desliming step. These fine particles are generally considered to be "platy" whereas the coarse particles are considered as being "blocky". If the defined coarse kaolin is fluid, i.e., Hercules viscosity greater than 250 rpm at 18 dynes, at 65-75% solids concentration, then it alone is the product of the invention. If the defined coarse kaolin is not fluid, i.e., Hercules viscosity is less than 250 rpm at 18 dynes, at 65-75% solids, then a component of very fluid and blocky fine kaolin clay is added to the defined coarse kaolin. This fine kaolin clay component is made preferably using a selective flocculation or a magnetic separation process. The inventors have discovered that by replacing the platy fine particles removed from the coarse kaolin in the defining step with the blocky

and fluid fine kaolin clay attains the desired improved rheological properties for the water-clay slurry.

In a preferred embodiment of the invention, the coarse kaolin clay alone is used as the kaolin clay pigment of the invention.

Further processing of this coarse kaolin clay may involve leaching and filtering. These processes are well known to those skilled in the art and are standard processes for the beneficiation of a kaolin clay

The coarse kaolin clay produced as discussed hereinabove has the physical properties shown in Table 1.

**Table 1**

<b>Slurry:</b>	
Solids, %	60-70
Brookfield Viscosity, #2 Spindle @ 20 rpm	200 cps or greater
Hercules Viscosity, @ 18 dynes	less than 1200 rpm
<b>Particle Sized Distribution</b>	
% < 10 u	99.6 - 99.9
% < 5 u	99.7 - 99.8
% < 2 u	90 - 96
% < 1 u	73 - 82
% < 0.5 u	49 - 58
% < 0.25 u	15 - 30
Brightness (G.E.)	89.0 - 92.0
b-value	2.66
TiO <sub>2</sub> %	0.728
Fe <sub>2</sub> O <sub>3</sub> %	0.266
Particle Shape Factor	12 - 25

From Table 1, it can be seen that the G.E. brightness of the kaolin clay is at least 89.0; the particle size distribution is such that at least 90% by weight of the particles have an equivalent spherical diameter less than 2  $\mu$ m;

and not more than 30% by weight of the particles have an equivalent spherical diameter less than 0.25  $\mu\text{m}$ . As stated hereinabove, this coarse kaolin clay generally will have a high percentage of "blocky" particles at the coarse end and a small amount of "platy" particles at the fine end whereby the shape factor of the whole clay will be greater than 12, and preferably ranging from 12-25, more about which will be discussed hereinabove.

This coarse kaolin clay of Table 1 has been shown at times to produce a viscous, low fluidity slurry for a high solids coating application which may be unsatisfactory to the papermakers. In order to obtain the desired rheology in the slurry, according to the teachings of the invention and as discussed hereinabove, a second aspect of the invention involves adding to the slurry a fine kaolin clay which may be made using a selective flocculation process.

This fine kaolin clay component of the pigment of the invention preferably can be produced by the following beneficiation process:

A blocky crude kaolin clay with a Hinckley Crystallinity Index less than 0.5 is blunged and dispersed at a slurry solids of from 50 to 70% by weight. The dispersants are a combination of sodium hexametaphosphate and sodium silicate. The dispersed clay slurry is passed through a high shear mixer and then degritted to remove 100+ mesh particles. After fully dispersing and degritting the clay slurry, the slurry is diluted to 20 to 40% solids, preferably 30% solids by weight.

This diluted slurry is metered into a high intensity wet magnetic separator for removal of the iron-bearing impurities. The product from this process is then diluted to 25% solids by weight and the impurities are discarded.

The diluted slurry at 25% solids is then treated with 10 to 25% by weight sodium chloride solution added at a rate of 5 to 40 lbs./dry ton clay, with 20 lbs./dry ton clay being typical. The diluted slurry is subjected to a selective flocculation process. In this process, the diluted slurry is treated with a high molecular weight anionic polymer in a dosage of 0.01 to 0.5 lbs./dry ton of clay in a 0.02 to 0.1% solution. The high molecular weight anionic polymer has a molecular weight in excess of one million, and

preferably in the range of 10 to 15 million, and preferably is a copolymer of a polyacrylamide. The high molecular weight anionic polymer may be any one of those commercially available.

In this selective flocculation process, the impurities are flocced out of suspension while the kaolin clay remains in suspension. The refined clay slurry may be ozoned, bleached, and/or filtered, followed by either redispersing in a makedown tank or alternately spray dried.

This fine kaolin clay component produced by the above process has a TAPPI brightness greater than 89.0, i.e., ranging from about 90.0 to about 93 and a rheology of less than 10 dynes at 4400 rpm at 70% solids; a particle size distribution (p.s.d.) such that 95% by weight of the particles have an e.s.d. less than 2 microns and about 50-75% by weight of the particles have an e.s.d. less than 0.25 micron.

In a second aspect of the invention, this fine kaolin clay component is used when necessary and is blended with the coarse clay in amounts ranging from 0.1 % to 30.0% by weight of the blend to give a rheology of 18 dynes at 250 rpm or better at 65-75% solids. This blend will have a shape factor greater than 12, and preferably ranging between 12 and 25.

A suitable fine kaolin clay component for use in the invention may be that produced according to the teachings of U.S. Serial No. 08/876,523 filed on June 11, 1997 entitled "Method For Separating Mixture Of Finely Divided Minerals And Product Thereof", William L. Garforth et al., and assigned to the assignee of the present invention, which is incorporated herein by reference.

In the invention, the fine kaolin clay component, either in dry form or in slurry form, is blended with the coarse kaolin clay either in slurry form or in dry form. The amount of the kaolin clay will range from about 0.1% by weight to about 30% by weight of the solids, more preferably between about 5% to about 25% by weight, and most preferably about 7% to about 13% by weight of the solids. Preferably, the solids in the slurry will range from about 65% to 75% by weight of the slurry. If in dry form, the kaolin clay particles are blended together in slurry form and then spray dried.



In the invention, the coarse kaolin clay is optionally combined with the fine kaolin clay to produce a kaolin clay pigment where the ratio of % finer than 2 microns (92%) divided by the % finer than 0.25 micron (30%) is equal to or greater than 3. The kaolin clay pigment of the invention preferably has a particle size distribution "p.s.d." such that at least 90% by weight of the particles have an e.s.d. smaller than 2  $\mu\text{m}$  and not more than 30% by weight of the particles have an e.s.d. smaller than 0.25  $\mu\text{m}$ . This pigment is fluid at high solids concentration, i.e., 65-75% solids. The shape factor for the pigment ranges from 12 to 25.

A kaolin product of high shape factor is considered to be more "platy" than a kaolin product of low shape factor. "Shape factor" as used herein is a measure of an average value (on a weight average basis) of the ratio of mean particle diameter to particle thickness for a population of particles of varying size and shape as measured using the electrical conductivity method and apparatus described in U.S. Patent Nos. 5,128,606 and 5,516,617, and using the equations derived in these patent specifications. "Mean particle diameter" is defined as the diameter of a circle which has the same area as the largest face of the particle. In the measurement method described in U.S. Patent No. 5,128,606, electrical conductivity of a fully dispersed aqueous suspension of the particles under test is caused to flow through an elongated tube. Measurements of the electrical conductivity are taken between (a) a pair of electrodes separated from one another along the longitudinal axis of the tube, and (b) a pair of electrodes separated from one another across the transverse width of the tube, and using the difference between the two conductivity measurements the shape factor of the particulate material under test is determined.

As will be appreciated by those skilled in the art, the particle-size distribution (p.s.d.) of a particular product such as the kaolin clay pigment of the invention may be determined by measuring the speeds at which the dispersed particles of the particular clay under testing, sediment through a standard dilute aqueous suspension using a Sedigraph<sup>TM</sup> machine, e.g. Sedigraph 5100, obtained from Micromeritics Corporation, U.S.A. The size of

the given particle is expressed in terms of the diameter of a sphere of equivalent diameter, which sediments through the suspension, is expressed as the equivalent spherical diameter or e.s.d. The Sedigraph™ machine graphically records the percentage by weight of particles having e.s.d. less than a certain e.s.d. value versus e.s.d.

The invention uses the BET method using N<sub>2</sub> as adsorbate to determine the surface area.

The kaolin clay pigment of the invention has particular application in a coating formulation in coating groundwood or free sheet printed paper. As such, the coating composition generally is in the form of an aqueous suspension or slurry and comprises the kaolin clay pigment of the invention, a hydrophilic adhesive or binder, a latex, a cross-linker, an insolubilizer and an optical brightening agent (OBA).

The binder level may range from e.g., 4% by weight to 20% by weight, and may comprise an adhesive derived from natural starch obtained from a known plant source, for example, wheat, maize, etc., or could be starch. The latex level may range from 4% by weight to 20% by weight and may be selected from the group consisting of styrene butadiene, acrylic latex, vinyl acetate latex, or styrene acrylic copolymers.

The insolubilizer level may be up to 2% by weight.

The cross-linker level may be up to 5% by weight and selected from the group consisting of glyoxals, melamine formaldehyde, resins, and ammonium zirconium carbonates. The optical brightness agent level may be up to 1% by weight and an example is stilbene derivatives.

For the above additives, the percentages by weight are based on the dry weight of pigment (100%) present in the composition.

The coating comprising the kaolin clay pigment of the invention may be applied to the base paper to coat the paper and calendered to form the gloss coating thereon. The coating may be formed on one side or on both sides of the paper, and preferably is added on both sides.

Calendering is a well known process in which paper smoothness, gloss, and printed gloss are improved and bulk is reduced by passing a

coated paper sheet between calender nips or rollers one or more times. Usually, elastomer coated rolls are employed to give pressing of high solids compositions. An elevated temperature may be applied. Five or more passes through the nips may be applied.

The paper after coating and calendering may have a total weight per unit area in the range  $30 \text{ g.m}^{-2}$  to  $70 \text{ g.m}^{-2}$ , especially  $49 \text{ g.m}^{-2}$  to  $65 \text{ g.m}^{-2}$  or  $35 \text{ g.m}^{-2}$  to  $48 \text{ g.m}^{-2}$ . The final coating preferably has a weight per unit area preferably from  $3 \text{ g.m}^{-2}$  to  $20 \text{ g.m}^{-2}$ , especially from  $5 \text{ g.m}^{-2}$  to  $13 \text{ g.m}^{-2}$ . Such a coating may be applied to both sides of the paper. The paper gloss may range from 50 to 90 TAPPI units at 75 degree angle of measurement, the print gloss may range from 20 to 60 TAPPI units at 20 degree angle of measurement and 85 to 100 TAPPI units at 75 degree angle of measurement, and the Parker Print Surf value at a pressure of 1 mPa of each paper coating may be less than  $1 \mu\text{m}$ .

The brightness of the pigments are determined in the conventional manner (TAPPI Standard T 452 m-58) using a U.S. Brightness Meter.

The gloss of a coated paper surface may be measured by means of a test laid down in TAPPI Standard No. 480 ts-65. The intensity of light reflected at an angle from the surface of the paper is measured and compared with a standard of known gloss value. The beams of incident and reflected light are both at an angle of  $75^\circ$  to the normal to the paper surface. The results are expressed in TAPPI gloss units.

The print gloss of a coated paper surface may be measured through a standard TAPPI test. The intensity of light reflected at an angle from the surface of the paper is measured and compared with a standard known print gloss value. The beams of incident and reflected light are both at an angle of  $20^\circ$  or  $75^\circ$  to the normal to the paper surface. The results are expressed in TAPPI print gloss units. As an example in one coating formulation as a result of the invention, the coated sheet had a paper gloss ranging between 77 to 83, and a print gloss ranging from 35 to 60 at 20 degree angle of measurement.

The Parker Print Surf test provides a measure of the smoothness of a paper surface, and measures the rate at which air under pressure leaks from a sample of the coated paper which is clamped, under a known standard force, between an upper plate which incorporates an outlet for the compressed air and a lower plate, the upper surface of which is covered with a sheet of either a soft or a hard reference supporting material according to the nature of the paper under test. From the rate of escape of the air, a root mean cube gap in  $\mu\text{m}$  between the paper surface and the reference material is calculated. A smaller value of this gap represents a higher degree of smoothness of the surface of the paper under test.

The kaolin clay pigment of the present invention will be better appreciated, and the process for producing the clay pigment of the invention will be better understood with reference to the examples hereinafter which are to be regarded as illustrative, not limiting, of the present invention.

The following examples illustrate a kaolin clay pigment having the desired physical properties and exceptional advantages in coating applications.

#### Example 1

This Example involved a coarse clay (Product A) having the characteristics shown in Table 1. A crude kaolin clay with a Hinckley Index of about 0.8 was blunged in water with sodium hexametaphosphate to form an aqueous kaolin suspension as hereinbefore described. This suspension was then subjected to a froth flotation to remove titanium containing impurities in the froth. This slurry was then subjected to classification in a Bird centrifuge where the particles generally would have a particle-size distribution of 89-96% by weight less than 2.0 microns, and which in this Example 1 had a particle size distribution of 95% by weight less than 2.0 microns.

The classified kaolin suspension was subjected to delamination in a sand grinder. The grinding medium in the sand grinder is of relatively high specific gravity and comprises grains of silica sand having diameters ranging from 0.25 mm to 2.0 mm. The sand grinder comminuted the kaolin clay to give individual thin, substantially hexagonal plates. This process increased

the shape factor of the kaolin clay to the preferred shape factor of 12 or greater. The kaolin suspension was then subjected to a defining step by centrifuging in a disc-nozzle centrifuge equipped with internal recycle manufactured by Dorr-Oliver Incorporated of Stamford, CN. The fine fraction was discarded. The coarse fraction contained 17.8% by weight of fines, i.e., less than 0.25 micron. This coarse fraction in slurry form was subjected to leaching. After leaching, filtering (dewatering on a rotary vacuum dryer), rinsing and redispersing, the coarse kaolin clay was admixed in a conventional manner with binders etc. and formed into a dispersed coating clay formulation commercially used for offset paper and compared to a top grade commercial kaolin pigment in a coating clay formulation.

The results are shown in Table 2.

**Table 2**

	Product A	Top Grade Commercial Pigment
<b>Pigment Properties</b>		
Brightness (G. E.)	91.4	91.1
Particle Size - % < 2 $\mu\text{m}$	93.0	92.0
Particle Size - % < 0.25 $\mu\text{m}$	17.8	21.0
Shape Factor	18.4	17.6
BET ( $\text{m}_2/\text{g}$ )	17.1	11.5
Brookfield @ 20 rpm (c.p.s.)	500	335
Hercules @ 18 dynes (rpm)	360	880
% Solids	70	70
<b>Offset Coated Sheet Properties</b>		
Brightness (G.E.)	87.4	87.3
Opacity	93.4	93.0
Gloss (75°)	79.6	77.8
Print Gloss (75°)	86.2	84.7
Parker Print Surf (PPS)	0.75	0.84

Properties shown at 15 gsm coat weight

As evident from Table 2, Product A exhibited improved brightness, opacity, gloss, print gloss, and PPS (smoothness) when compared to the commercial coating clay in offset coating formulations. Also, the surface area of Product A was greater than that of the commercial coating clay, i.e., 17.1 BET surface area vs. 11.5 BET surface area.

#### Example 2

This Example involved a coarse clay (Product B) having the characteristics shown in Table 1. Crude kaolin clay with a Hinckley Index of about 1.0 was blunged in water similar to that of Example 1. After blunging, the suspension was subjected to a selective flocculation to remove the titanium containing impurities. In this selective flocculation, a high molecular weight anionic polymer, i.e., a copolymer of polyacrylamide was used to floc out the pure kaolin while leaving the discolored impurities in suspension. The flocculated kaolin was mixed at a high shear rate and its suspension was subjected to ozonation, as described hereinabove, and then subjected to classification to produce a product with a p.s.d. of 93% by weight less than 2.0 microns, sand grinding to obtain a shape factor of at least 12 for the kaolin clay, defining, leaching and filtering under the same conditions as described in Example 1. As a result of the defining process, only 20% of the kaolin particles in the coarse fraction were less than 0.25 microns.

Similar to Example 1, Product B was incorporated into a coating formulation in a conventional manner commonly used for offset paper and compared to the top grade commercial pigment used in Example 1.

The results are shown in Table 3.

**Table 3**

	Product B	Top Grade Commercial Pigment
<b>Pigment Properties</b>		
Brightness (G.E.)	90.7	91.1
Particle Size - % < 2 $\mu\text{m}$	94.0	92.0
Particle Size - % < 0.25 $\mu\text{m}$	20.0	21.0
Shape Factor	15.4	17.6
BET ( $\text{m}_2/\text{g}$ )	14.1	11.5
Brookfield @ 20 rpm (c.p.s.)	688	335
Hercules @ 18 dynes (rpm)	165	880
% Solids	70	70
<b>Offset Coated Sheet Properties</b>		
Brightness (G.E.)	84.5	84.4
Opacity	93.1	93.3
Gloss (75°)	81.3	80.6
Print Gloss (20°)	55.5	50.3
(PPS)	0.77	0.80

Properties shown at 15 gsm coat weight

As evident from Table 3, Product B exhibited improved brightness, gloss, and print gloss when compared to the commercial coating clay in offset formulations. Also, the pigment of Product B had a greater surface area than the commercial coating clay, i.e., 14.1 BET surface area vs. 11.5 BET surface area.

### Example 3

This Example involved a blend of a coarse kaolin clay with a fine kaolin clay in accordance with the teachings of a second embodiment of the invention.

A coarse kaolin clay (Product B of Example 2) was blended with a fine kaolin clay component. This fine kaolin clay component had a Hinckley Index

of about 0.4 and was produced according to the teachings of the aforesaid U.S. Serial No. 08/876,523 filed June 16, 1997.

These two kaolin clays were blended together in slurry form in the weight percent solids shown in Columns 2-4 of Table 4 and then admixed in a coating formulation for evaluation in an offset process and compared to the top grade commercial coating clay of Examples 1 and 2. The particle shape factor for these blends of clays was greater than 12 as shown in Table 4. The coating formulation was the same as that used in Examples 1 and 2.



The results are shown in Table 4.

**Table 4**

Pigment Properties Of The Blends						
Blend #		1	2	3	4	
% Coarse Kaolin Clay	0%	100%	95%	90%	80%	Top Grade Commercial Pigment
% Fine Kaolin Clay	100%	0%	5%	10%	20%	
Brightness (G.E.)	91.0	90.9	90.9	90.9	90.8	91.1
Particle Size - % < 2 $\mu$ m	99.4	91.7	93.3	93.5	94.2	92.0
Particle Size - % < 0.25 $\mu$ m	67.5	18.8	20.7	22.0	26.3	21.0
BET ( $m^2/g$ )	--	15.4	15.7	15.6	16.1	11.5
Brookfield @ 20 rpm (c.p.s.)	200	350	325	300	300	335
Hercules @ 18 dynes (rpm)	4.5*	220	230	340	500	880
% Solids	70	70.3	70.3	70.3	70.3	70
Shape Factor	16.4	15.4	14.2	13.7	12.5	
* dynes @ 4400 rpm						
Offset Coated Sheet Properties						
Blend #			2	3	4	
% Coarse Kaolin Clay			95%	90%	80%	
% Fine Kaolin Clay			5%	10%	20%	
Brightness (G.E.)			84.6	84.4	84.5	84.2
Opacity			93.6	93.8	93.7	93.6
Gloss (75°)			80.0	81.0	80.8	80.0
Print Gloss (20°)			47	48	44	44
PPS 10 ( $\mu$ m)			0.87	0.84	0.84	0.82

Properties shown at 15 gsm coat weight

As evident in Table 4, the blends of kaolin clays in offset coated sheet exhibited improved brightness, opacity, gloss, and print gloss when compared to the commercial coating clay. Also, the surface area of the pigment of the blends was greater than that of the commercial clay.

The properties of the kaolin clay pigment of the invention are: the particle size distribution is such that at least 90% by weight of the particles have an e.s.d. finer than 2  $\mu\text{m}$  and less than 30% by weight having an e.s.d. finer than 0.25  $\mu\text{m}$ . The ratio of % finer than 2 microns divided by the % finer than 0.25 micron is equal to or greater than 3.0. The surface area is at least 12.0  $\text{m}^2/\text{g}$  (BET method using nitrogen as adsorbent); the Hercules viscosity is greater than 250 rpm at 18 dynes at a solids ranging from 65% to 75% solids; and the shape factor is 12 or greater.

The kaolin clay pigment of the invention has been found to produce substantial advantages in opacification, glossing, smoothness, and printability in paper coating applications when compared to other commercial kaolin pigments. This composition has "good" fluidity at a high solids concentration (>69.1% solids) and at both high and low shear rates is highly desirable by papermakers because of enhanced productivity.

Whereas particular embodiments of the present invention have been described for purposes of illustration, it will be evident to those skilled in the art that numerous variations and details of the invention may be made without departing from the invention as defined in the appended claims.

### Claims

1. A kaolin clay pigment for use in a coating formulation for paper, said kaolin clay pigment comprising kaolin clay and having the following characteristics:

(1) Particle size (e.s.d. as determined by Sedigraph)

(a) less than 2 microns : at least 90%;  
less than 0.25 microns: less than 30%  
% less than 2 microns

Ratio =  $\frac{\% \text{ less than 0.25 microns}}{\% \text{ less than 2 microns}} \geq 3.0$

(2) Surface area : at least 12.0 m<sup>2</sup>/g or more (BET method using N<sub>2</sub> as adsorbent);

(3) Particle shape factor : 12 or greater; and

(4) Hercules viscosity : measured at 250 rpm or better fluidity and 65% to 75% solids at 18 dynes.

2. A kaolin clay pigment of Claim 1 wherein said kaolin clay comprises low-defect kaolinite and has a Hinckley Crystallinity Index greater than 0.6.

3. A kaolin clay pigment of Claim 1 wherein said kaolin clay pigment comprises a coarse kaolin clay which has been subjected to a froth flotation step.

4. A kaolin clay pigment of Claim 1 wherein said kaolin clay pigment comprises a coarse kaolin clay which has been subjected to a selective flocculation step.

5. A kaolin clay pigment of Claim 1 wherein said kaolin clay pigment comprises a coarse kaolin clay and a fine kaolin clay having a p.s.d. where about 90-99.9% by weight has an e.s.d. less than 2 microns and about 50-75% by weight has an e.s.d. less than 0.25 micron.

6. A kaolin clay pigment of Claim 5 wherein said fine kaolin clay contains high-defect kaolinite and has a Hinckley Crystallinity Index less than 0.5.

7. A kaolin clay pigment of Claim 5 wherein said fine kaolin clay is blended with said coarse kaolin in amounts ranging from about 0.1 to about 30% by dry weight of said kaolin clay pigment.

8. A kaolin clay pigment of Claim 1 exhibiting improved optical and physical properties in said coating formulation when applied to said paper.
9. A paper coated with the kaolin clay pigment of Claim 1 having a brightness gain ranging from 0.1 to 2 units; an opacity gain ranging from 0.1 to 1.0 unit; a print gloss gain (75°) ranging from 0.1 to 8 units; and a sheet gloss gain ranging from 0.1 to 4.0 units.
10. A paper coating composition comprising a dispersed kaolin clay pigment comprising kaolin clay and having the following characteristics:
- (1) Particle size (e.s.d. as determined by Sedigraph)
    - (a) less than 2 microns : at least 90%;  
less than 0.25 microns : less than 30%  
% less than 2 microns  
Ratio = % less than 0.25 microns  $\geq$  3.0
  - (2) Surface area : at least 12.0 m<sup>2</sup>/g or more (BET method using N<sub>2</sub> as adsorbent);
  - (3) Particle shape factor : 12 or greater; and
  - (4) Hercules viscosity : measured at 250 rpm or better fluidity and 65% to 75% solids at 18 dynes.
11. A paper coating of Claim 10 wherein said kaolin clay pigment comprises a coarse kaolin clay subjected to a froth flotation step.
12. A paper coating of Claim 10 wherein said kaolin clay pigment comprises a coarse kaolin clay subjected to a selective flocculation step.
13. A paper coating of Claim 10 wherein said kaolin clay pigment comprises a coarse kaolin clay and a fine kaolin clay having a p.s.d. where about 90-99.9% by weight has an e.s.d. less than 2 microns and about 50% to 75% by weight has an e.s.d. less than 0.25 micron.
14. A paper coating of Claim 13 wherein said fine kaolin clay is blended with said coarse kaolin in amounts ranging from about 0.1 to about 30% by dry weight of said kaolin clay pigment.
15. A paper coating of Claim 14 wherein said coarse kaolin clay contains a low-defect kaolinite and has a Hinckley Crystallinity Index greater than 0.6

and wherein said fine kaolin clay contains a high-defect kaolinite and has a Hinckley Crystallinity Index less than 0.5.

16. A method for producing a kaolin clay pigment with improved rheological properties for a high solids clay slurry, the steps comprising:

- (a) blunging a coarse crude kaolin clay containing a low defect kaolinite and having a Hinckley Crystallinity Index greater than 0.6 in water with a dispersant to form an aqueous slurry with a solids level ranging from about 50% to 70% by weight of said slurry;
- (b) removing particles above 45 microns and impurities from the clay slurry;
- (c) classifying the clay slurry to a particle size distribution such that 89% to 96% by weight of the particles have an e.s.d. less than 2 microns;
- (d) subjecting said clay slurry to a delamination step to produce clay having a particle size distribution such that 90% to 97% by weight of the particles have an e.s.d. less than 2 microns and a shape factor equal to or greater than 12;
- (e) subjecting said clay slurry to a defining step to produce a coarse fraction and a fine fraction; and
- (f) discarding said fine fraction of step (e),  
said coarse fraction having a Hercules viscosity greater than 250 rpm at 18 dynes at a solids ranging from about 65% to 75% for use as said kaolin clay pigment.

17. A method for producing a kaolin clay pigment with improved rheological properties, the steps comprising:

- (a) blunging a coarse crude kaolin clay containing a low-defect kaolinite and having a Hinckley Crystallinity Index greater than 0.6 in water with a dispersant to form an aqueous slurry with a solids level ranging from about 50% to 70% by weight of said slurry;
- (b) removing particles above 45 microns and impurities from the clay slurry;
- (c) classifying the clay slurry to a particle size distribution such that 89% to 96% by weight of the particles have an e.s.d. less than 2 microns;

(d) subjecting said clay slurry to a delamination step to produce clay having a particle size distribution such that 90% to 97% by weight of the particles have an e.s.d. less than 2 microns and a shape factor equal to or greater than 12;

(e) subjecting said clay slurry to a defining step to produce a coarse fraction and a fine fraction;

(f) discarding said fine fraction of step (e); and

(g) selectively admixing a percentage of a fine kaolin clay to said coarse fraction of step (e) to improve the fluidity of said clay and to produce a clay slurry having a Hercules viscosity greater than 250 rpm at 18 dynes at a solids ranging from about 65% to about 75%.

18. A method of Claim 17 wherein said fine kaolin clay has a particle size distribution such that 90-99.9% by weight has an e.s.d. less than 2 microns and 50% to 75% by weight has an e.s.d. less than 0.25 micron.

19. A method of Claim 18 wherein said fine kaolin clay is produced through a beneficiation process which includes a selective flocculation step for removing the impurities in the clay.

20. A method of Claim 17 wherein said percentage of said fine kaolin clay is admixed with said coarse clay in an amount ranging from 0.1% to 30.0% by weight of the kaolin clay pigment.

21. A method of Claim 17 wherein said percentage of said fine kaolin clay is blended with said coarse fraction of said clay slurry to form said kaolin clay pigment.

22. A method of Claim 17 wherein said fine kaolin clay contains a high-defect kaolinite having a Hinckley Crystallinity Index less than 0.5.

## INTERNATIONAL SEARCH REPORT

Inventor and Applicant No.

PCT/US 99/28189

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09C1/42 D21H19/40

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09C C04B D21H B03B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 112 782 A (ENGELHARD CORPORATION) 12 May 1992 (1992-05-12) column 4, line 22 - line 59 claims 1-15; tables 1,2 figure 1	1,8-10
A	US 5 169 443 A (ENGELHARD CORPORATION) 8 December 1992 (1992-12-08) cited in the application column 2, line 54 - column 4, line 68; claims 1-4; example 2	1-22
A	US 5 749 958 A (EGLEHARD CORPORATION) 12 May 1998 (1998-05-12) claims 1-8; examples 4-6,10,11	1-22



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/28189

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